ELSEVIER

Journal of Molecular Catalysis A: Chemical 99 (1995) 77–86

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Oxidation of olefins by palladium(II). Part XIV [1]. Product distribution and kinetics of the oxidation of ethene by $PdCl_3(pyridine)^-$ in aqueous solution in the presence and absence of $CuCl_2$: a modified Wacker catalyst with altered reactivity

John W. Francis, Patrick M. Henry *

Department of Chemistry, Loyola University of Chicago, Chicago, IL 60626, USA

Received 10 November 1994; accepted 10 February 1995

Abstract

In the absence of $CuCl_2$, ethene was oxidized to ethanal by $PdCl_3(pyridine)^-$ in aqueous solution by the rate expression: $-d[C_2H_4]/dt = k'K'[PdCl_3(Py)^-][C_2H_4]/[H^+][Cl^-]^2$ where K' is the equilibrium constant for π-complex formation between ethene and $PdCl_3(Py)^-$ (Py = pyridine). This rate expression is of the same form as that previously found for the oxidation of ethene by $PdCl_4^{2-}$ in aqueous solution (Wacker reaction). The value of K' for $PdCl_3(Py)^-$ was found to be 20.3 which is close to the value of 17.4 previously measured for π-complex formation between ethene and $PdCl_4^{2-}$. However, the value of k for $PdCl_4^{2-}$ was 750 times the value of k' for $PdCl_3(Py)^-$. This result suggests that the hydroxypalladation adduct from $PdCl_3(Py)^-$ is much more stable towards decomposition to ethanal than the corresponding one from $PdCl_4^{2-}$. A direct result of this higher stability is the expectation that the adduct from $PdCl_3(Py)^-$ should be more readily intercepted by $CuCl_2$ to produce 2-chloroethanol. At chloride concentrations as low as 0.2 M and $[CuCl_2] = 4$ M, the product was almost 50% 2-chloroethanol. At $[CuCl_2] = 8$ M, the product was 98% 2-chloroethanol. With $PdCl_4^{2-}$, a chloride concentration of 3 M is required before an appreciable amounts of 2-chloroethanol are produced at any cupric chloride concentration. For the reaction of ethene with $PdCl_4^{2-}$, these results are consistent with a mechanism involving cis addition at low $[Cl^-]$ and trans addition at high $[Cl^-]$. The pathway for ethanal formation may be different with $PdCl_3(Py)^-$ than it is with $PdCl_4^{2-}$.

Keywords: 2-Chloroethanol; Copper(II) chloride; Ethene; Oxidation; Palladium(II); Modified catalyst; Wacker catalyst

1. Introduction

The mechanism of the aqueous $PdCl_4^{2-}$ catalyzed oxidation of ethene to ethanal (Wacker reaction) has generated considerable controversy. The rate expression under low $[Cl^-]$ conditions was found to be given by Eq. 1 [2].

$$\text{rate} = k[PdCl_4^{2-}][\text{olefin}]/[H^+][Cl^-]^2 \quad (1)$$

The $1/[Cl^-]^2$ term must arise from the two pre-equilibria shown in Eqs. 2 and 3.

$$PdCl_4^{2-} + \text{olefin} \overset{K_1}{\rightleftharpoons} PdCl_3(\text{olefin})^- + Cl^- \quad (2)$$

$$PdCl_3(\text{olefin})^- + H_2O \overset{K_2}{\rightleftharpoons} PdCl_2(H_2O)(\text{olefin}) + Cl^- \quad (3)$$

(1a)

* Corresponding author. Fax. (+1-312)5083086.

[1] For Part XIII see ref. [1].

SSDI 1381-1169(95)00041-0

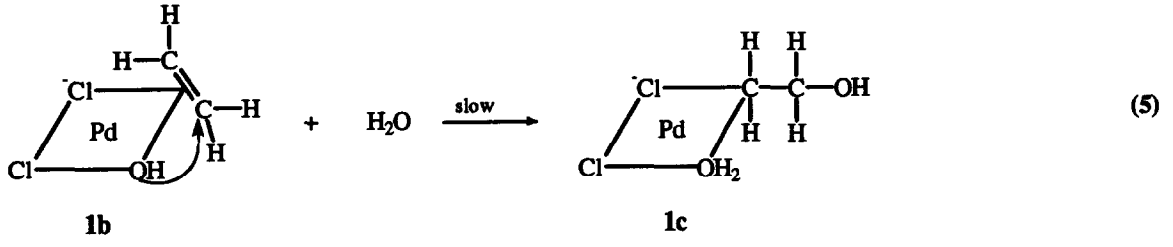
The dispute in the Wacker process involves the source of the proton inhibition term. This term could be explained by routes involving either cis or trans addition to a Pd(II)–π-complex. Based on the kinetics and deuterium isotope effects a mechanism involving the proton inhibition resulting from the acid dissociation shown in Eq. 4 followed by cis attack of coordinated hydroxide shown in Eq. 5 (Scheme 1) [3].

$$\underset{\mathbf{1a}}{PdCl_2(H_2O)(olefin)} \overset{K_a}{\rightleftharpoons} \underset{\mathbf{1b}}{PdCl_2(OH)(olefin)^-} + H^+ \qquad (4)$$

However, more recent stereochemical studies have suggested that, in fact, the addition of Pd(II) and hydroxyl is a trans process. Thus, at high $[Cl^-]$ (>3 M), 2-chloroethanol becomes a major product [4]. Making use of this fact, in a very elegant stereochemical study, (*E*)- and (*Z*)-ethene-d_2 were oxidized at high $[Cl^-]$ (3.3 M) in the $CuCl_2$ promoted reaction to give 2-chloroethanol-d_2 [5]. The configurations of the chloroethanols obtained from the two deuterated ethenes was consistent only with trans hydroxypalladation. Based on these studies, presently the generally accepted mechanism for the Wacker reaction involves trans attack on a Pd(II)–ethene π-complex as shown in Eq. 6 (Scheme 2).

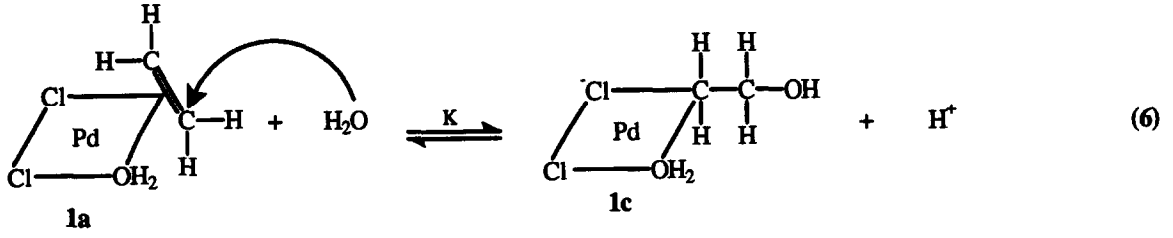
However, there is now a growing body of evidence that there are two modes of addition: one that predominates at low $[Cl^-]$ and another that predominates at high $[Cl^-]$. Furthermore the two modes of addition apparently have opposite stereochemistries. Thus, allyl alcohol-1,1- and 3,3-d_2, are oxidized to Wacker products [6] by the rate expression given by Eq. 1 at low $[Cl^-]$ [7]. However, at $[Cl^-] > 2.0$ M, these allyl alcohols undergoes a non-oxidative isomerization and solvent exchange which obeys the rate expression given by Eq. 7 [8].

$$\text{rate} = k[PdCl_4^{2-}][\text{olefin}]/[Cl^-] \qquad (7)$$



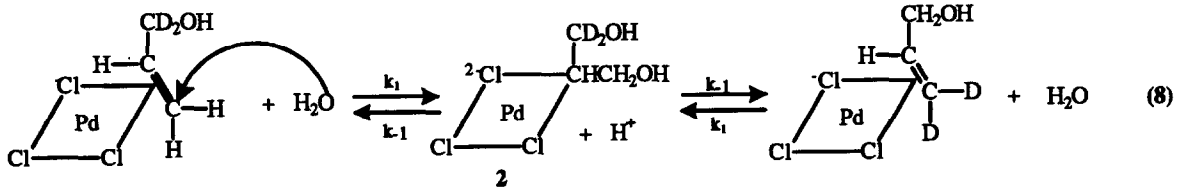
(5)

Scheme 1.



(6)

Scheme 2.



(8)

Scheme 3.

This rate expression is consistent with trans attack on an trichloropalladium(II)–olefin π-complex. The reaction scheme is shown in Eq. 8 (Scheme 3) where the intermediate **2** cannot oxidatively decompose but can only reverse the hydroxypalladation to give isomerized allyl alcohol-d_2. Apparently, the reason **2** is stable to oxidative decomposition is the fact that it does not have a labile coordination site for hydride transfer which would initiate oxidative decomposition. Note that the intermediate **1c** in Eq. 5 *does* have a labile aquo containing coordination site. Furthermore, in two previous papers by the authors the kinetics and stereochemistry of the allylic isomerization of the tetrasubstituted allylic alcohol (*E*)-2-methyl-d_3-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol, **3a**, into an equilibrium mixture of **3a** and 2-methyl-4-methyl-d_3-1,1,1,5,5,5-hexafluoro-3-penten-2-ol, **3b**, in aqueous solution, was studied by ^1H and ^2H NMR, under conditions of both low (<1.0 M) [9] and high (>2.0 M) [10] chloride concentrations. The rate expression under low $[Cl^-]$ conditions was found to be given by Eq. 1 while the rate expression at high $[Cl^-]$ is given by Eq. 7. At low $[Cl^-]$ the results provided kinetic evidence for the route shown in Eq. 1. However the most significant result is that *stereochemistry of addition was different at low and high* $[Cl^-]$! Since both the kinetics and stereochemical studies with (*E*)- and (*Z*)-ethene-d_2 are consistent with trans addition at high $[Cl^-]$, the stereochemistry must be cis at low $[Cl^-]$ and trans at high $[Cl^-]$.

The general picture that emerges is that there are two modes of hydroxypalladation operative under all conditions in aqueous solution. One has a square chloride inhibition, and has cis stereochemistry, while the other has a first power chloride inhibition, and has trans stereochemistry. Because of the different order chloride inhibitions, the first is prevalent at low $[Cl^-]$ and the second predominates at high $[Cl^-]$. In regard to the stereochemical studies using the $CuCl_2$ promoted reaction, the intermediate **1c** is apparently too unstable towards oxidative decomposition to be intercepted by $CuCl_2$ to give 2-chloroethanol. On the other hand, the intermediate corresponding to **2** *is* stable enough to be intercepted by $CuCl_2$. Thus the stereochemical results at high $[Cl^-]$ does not give a true picture of the mode of addition at low $[Cl^-]$.

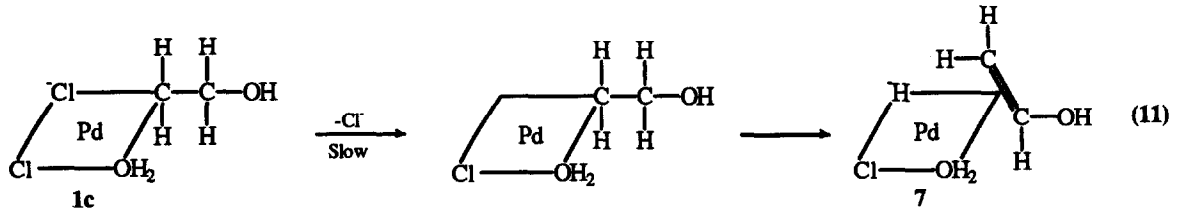
How can this mechanistic insight be used to design new catalytic systems? Note that the formation of the reactive species, **1a**, is inhibited by the equilibrium shown in Eq. 3. If a palladium(II) species is used which has even less tendency to form **1a** than the trichloropalladium(II)–π-complex in Eq. 3, the reaction leading to 2-chloroethanol should occur at lower $[Cl^-]$. A potential system is that where one chloride is replaced by a neutral ligand such as pyridine (Py) to give **4**. As shown in Eq. 9 the initially formed ethene Pd(II)–π-complex, **5**, is neutral. Thus, replacing a chloride with water would result in the positively charged aquo complex, **6** (Eq. 10).

$$\underset{\mathbf{4}}{PdCl_3(Py)^-} + C_2H_4 \overset{K_{1'}}{\rightleftharpoons} \underset{\mathbf{5}}{PdCl_2(PY)(C_2H_4)} + Cl^- \quad (9)$$

$$\underset{\mathbf{5}}{PdCl_2(Py)(C_2H_4)} + H_2O \overset{K_{2'}}{\rightleftharpoons} \underset{\mathbf{6}}{PdCl(H_2O)(Py)(C_2H_4)^+} + Cl^- \quad (10)$$

This would be an energetically unfavorable process. If the equilibrium forming **6** is discouraged then the attack on **5** by external water to give a hydroxypalladation adduct analogous to **2** in Eq. 8 will be promoted. As this adduct will have no labile coordination sites required for hydride shift to give ethanal, it will be stabilized towards this type of decomposition. Thus this adduct could possibly be stable enough to react with $CuCl_2$ to give 2-chloroethanol.

On the other hand the effects predicted for pyridine substitution on rate and product distributions for the trans hydroxypalladation route are quite different form those foreseen for the cis hydroxypalladation route. After formation of the intermediate, **1c**, according to Eq. 6, decomposition occurs by the route shown in Eq. 11 (Scheme 4)



Scheme 4.

[5] where the intermediate **7** decomposes to ethanal by generally accepted routes [5,11]. The rate determining loss of chloride is required to explain the deuterium isotope effects [11]. The important point to note is that coordinated water is not a reactant; *it only serves as a neutral ligand in the coordination sphere of Pd(II) to produce the neutral complex,* **1c**, *which is more readily attacked by external water than is the charged* $PdCl_3(C_2H_4)^-$ *species*. Now, if the only role of the aquo ligand is to produce a neutral complex, there appears to be no reason why pyridine could not replace water in the reaction scheme shown in Eqs. 6 and 11 without any change in mechanism. What might be expected in terms of rate expression and rates? Consider Eqs. 2 and 3 as compared to Eq. 9. The equilibria shown in Eqs. 2 and 3 are both needed to give the neutral complex, **1a**. The equilibria corresponding to Eq. 3 is not required with **4** because the equilibria shown in Eq. 9 directly gives the neutral complex **5**. One direct effect would be a change in rate expression. Since the equilibrium shown in Eq. 10 is not required, there should only be a 1st order $[Cl^-]$ inhibition and the rate expression should be that shown in Eq. 12.

$$\text{rate} = k[PdCl_3(Py)^-][C_2H_4]/[H^+][Cl^-] \qquad (12)$$

A second result is that an increase in overall rate would be predicted since the initial catalyst is a singly charged complex, **4**, rather than $PdCl_4^{2-}$. Thus $PdCl_4^{2-}$ must undergo the added equilibrium shown in Eq. 3 to form a neutral complex. The equilibrium constant for Eq. 3 is small so formation of **1a** is not favorable. Thus a detailed study of π-complex equilibria shown in Eqs. 2 and 3 indicate that K_2 is less than 0.01 [12], and has been estimated to be of the order of 10^{-3} [3], so only a small amount of the $PdCl_3(\text{olefin})^-$ present would be in the form of **1a**. The rate increase would depend on chloride concentration since the ratio of **1a** to $PdCl_3(C_2H_4)^-$ will depend on $[Cl^-]$. If K_1 and K_1' have about the same values, at $[Cl^-] = 0.2$ M, the overall rate should be about 50 to 500 times faster with **4** than with $PdCl_4^{2-}$. Finally, in the trans hydroxypalladation mechanism decomposition is initiated by chloride loss from the intermediate adduct analogous to **1c** (Eq. 11). This mechanism would not predict any special stabilization of the intermediate hydroxypalladation adduct so 2-chloroethanol production at lower $[Cl^-]$ would not be expected.

This paper will describe a study of the oxidation of ethene by **4** in aqueous acid solution to give ethanal and 2-chloroethanol.

2. Results

2.1. π-complex formation

The equilibrium constant for complex formation according to Eq. 9 was measured by initial olefin uptake using gas burets. Results are listed in Table 1. The results are consistent only with the equilibrium shown in Eq. 9. The value of 20.3 for K_1' is close to the value of 17.4 found for the analogous equilibrium with $PdCl_4^{2-}$, indicating the difference in charge is not an important factor in π-complex formation [3].

2.2. Oxidation kinetics

The oxidation of ethene to ethanal only occurred at low chloride concentrations (<0.2

Table 1
Studies of the initial ethene uptake in aqueous acid solution at 25°C by potassium trichloropyridine palladate(II), $KPdCl_3(Py)$: determination of K_1' [a]

Run	$[Cl^-]$	$10^4[PdCl_2(Py)C_2H_4]$	$10^3[(PdCl_3(Py)^-]$	$[Cl^-]_e$ [b]	K_1' [c]
1	1.0	4.10	9.59	1.00	20.4
2	0.8	5.02	9.50	0.801	20.1
3	0.6	6.58	9.34	0.601	20.2
4	0.4	11.1	8.89	0.401	23.9
5	0.2	18.9	8.11	0.202	22.4
6	0.1	26.0	7.40	0.108	17.4
7	0.05	41.0	5.91	0.054	17.9
Average					20.3

[a] Conditions: $[H^+]$ and [Pd(II)] were kept constant at 0.50 M, and 0.01 M. μ was maintained at 2.0 M with $LiClO_4$. Initial $[C_2H_4]$ was 2.1×10^{-3} M.
[b] $[Cl^-]_e$ is concentration of free chloride at equilibrium.
[c] Average of at least five runs.

M). The kinetics were measured by ethene gas uptake using benzoquinone to regenerate the Pd(II). Results are listed in Table 2 which gives the equilibrium concentrations of all reactants. Examination of the kinetic data indicates that the Wacker rate expression given in Eq. 1 is obeyed. Thus, in runs 8–10, where $[H^+] = 0.5$ M and $[PdCl_3(Py)^-]$ remains approximately constant, the value of k_{obs} increases by about a factor of 4 each time the $[Cl^-]$ is halved, indicating a $[Cl^-]^2$ inhibition term. In regard to the dependence on $[PdCl_3(Py)^-]$, consider runs 9, 11 and 12 for which $[Cl^-]$ is approximately constant and $[H^+] = 0.5$ M. As $[PdCl_3(Py)^-]$ is doubled in going from run 9 to 11, k_{obs} doubles while, when $[PdCl_3(Py)^-]$ is decreased by a factor of 4 in going from run 11 to run 12, k_{obs} decreases by a factor of 4. These results indicate a 1st order dependence on $[PdCl_3(Py)^-]$. In regard to the proton dependence, consider runs 9, 13 and 14, for which $[Cl^-]$ and $[PdCl_3(Py)^-]$ remain almost constant. In going from run 9 to run 13, $[H^+]$ is halved and k_{obs} is doubled, while in going from run 13 to 14, $[H^+]$ is increased by a factor of 4 and k_{obs} decreases by the same factor. Thus there is a first order proton inhibition.

In the present case the value of the π-complex formation constant, K_1' in Eq. 9, is known so the rate expression can be rewritten as follows:

$$-d[C_2H_4]/dt = k'[PdCl_2(Py)(C_2H_4)]/[H^+][Cl^-] = k'K_1'[PdCl_3(Py)^-][C_2H_4]/[H^+][Cl^-]^2 \quad (13)$$

where the brackets represent equilibrium concentrations. The equilibrium concentrations of $PdCl_2(Py)(C_2H_4)$ and the other reactants, given

Table 2
Kinetics for ethene oxidation catalyzed by potassium trichloropyridine palladate(II), in aqueous acid solution at low chloride concentrations [a]

Run	$[Cl^-]$ [b] M	$[H^+]$ [c] M	$[PdCl_3(Py)^-]$ 10^3 M	$[PdCl_2(Py)(C_2H_4)]$ 10^3 M	$10^8 k_{obs}$ s^{-1} [d]	$10^7 k'$ $M^2 s^{-1}$ [e]
8	0.202	0.5	8.3	1.7	0.36	2.1
9	0.103	0.5	7.0	2.5	1.35	2.8
10	0.054	0.5	5.4	4.4	5.1	3.1
11	0.106	0.5	14	5.7	2.9	2.7
12	0.102	0.5	3.5	1.5	0.71	2.4
13	0.103	0.25	7.5	2.5	2.75	2.8
14	0.103	1.0	7.5	2.5	0.65	2.7
15	0.031	0.5	4.2	5.8	22.3	6.0
16	0.054	0.1	5.6	4.4	27.0	3.3
Average						2.7 [f]

[a] Conditions: [quinone] = 0.2 M, $\mu = 2$ by addition of appropriate amounts of $LiClO_4$, $T = 25$°C. All runs were done under 1 atm of ethylene pressure.
[b] Added as LiCl.
[c] Added as $HClO_4$.
[d] Calculated as a 1st order reaction in ethene with correlation coefficients greater than 95%.
[e] $k' = k_{obs}[Cl^-][H^+]/[PdCl_2(Py)(C_2H_4)]$.
[f] Run 15 was not included in calculation of average.

Table 3
Product distribution for the oxidation of ethene with $PdCl_3(Py)^-$ in the presence of $CuCl_2$ [a]

$[CuCl_2]$	% Ethanal [b]	% 2-Chloroethanol [b]
0.0	100.0	0.0
1.0	100.0	0.0
4.0	52.8	47.2
5.0	32.0	68.0
6.0	17.0	83.0
8.0	2.0	98.0

[a] Conditions: $[Cl^-] = 0.2$ M, $[H^+] = 0.4$ M, $[Pd(II)] = 0.082$ M, $T = 25°C$. All runs were carried out under 1 atm of ethene pressure.
[b] Determined by ^1H NMR.

in Table 2, permit the calculation of k'. These values are given in the last column of Table 2. Thus, although k_{obs} varies by a factor of almost two powers of ten, with the exception of run 15, the value of k' varies less than 30% from the average of about $2.7 \times 10^{-7}\ M^2\ s^{-1}$. This is to be compared to $2.04 \times 10^{-4}\ M^2\ s^{-1}$ for $[PdCl_3(C_2H_4)^-]$ [3]. The larger variation of run 15 can be attributed to the very low chloride concentration. It is known that the rate expression deviates from Eq. 1 in chloride-starved systems [13].

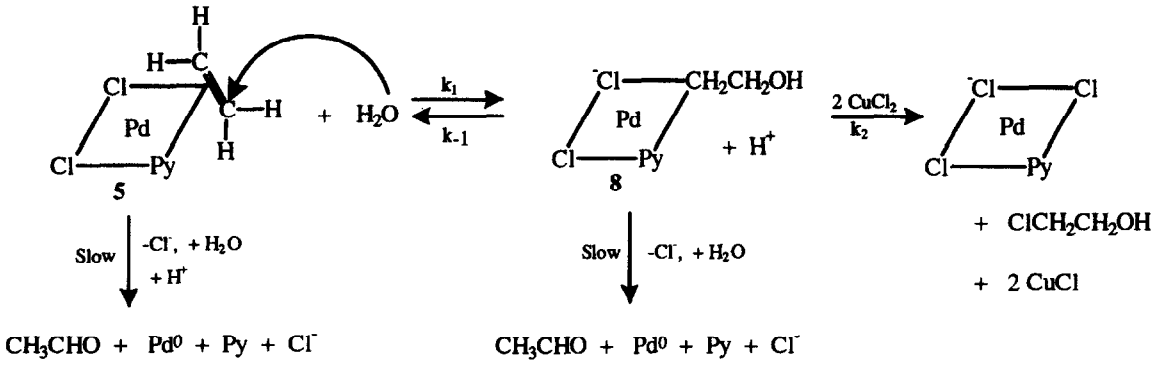
2.3. $CuCl_2$ promoted reaction

The competition between ethanal formation and 2-chloroethanol formation at $[Cl^-] = 0.2$ M and $[H^+] = 0.4$ M was determined at various cupric chloride concentrations. Results are given in Table 3. At $[CuCl_2] < 2.0$ M, ethanal, the expected Wacker product, was the only product detected. At concentrations of $CuCl_2$ greater than 4.0 M, a mixture of ethanal and 2-chloroethanol was found, with the amount of the alcohol increasing steadily with increasing $[CuCl_2]$ until at $[CuCl_2] = 8.0$ M, 2-chloroethanol is practically the only product.

3. Discussion

The present results clearly indicate that the mode of action of a catalyst can be drastically altered by relatively minor chemical modification. Thus, replacement of a chloride in the coordination sphere of Pd(II) by a neutral pyridine ligand: 1. reduces the value of the rate constant for the oxidation by a factor of about 750; and 2. makes the intermediate hydroxypalladation adduct stable enough to be intercepted by $CuCl_2$ to give 2-chloroethanol at chloride concentrations as low as 0.2 M. With $PdCl_4^{2-}$ a chloride concentration of at least 3 M is required before any appreciable amounts of 2-chloroethanol is formed [4]. This demonstration of the ability to change the reactivity of a catalyst by addition of neutral ligands is certainly the most important result of this paper.

A second important result involves the mechanism of the Wacker chemistry. As discussed in the Introduction, only the cis hydroxypalladation route would predict that a neutral ligand in the coordination sphere of Pd(II) would result in a retardation of the rate of a factor as large as 750. The trans addition mechanism, shown in Eqs. 6 and 11, on the hand would predict an increase in rate since the neutral π-complex, **5** (Eq. 9), should be present in considerably larger concentrations than the corresponding neutral π-complex, **1a** (Eq. 3), in the Wacker chemistry. In the present study it was shown that the π-complex formation constants, K_1 (Eq. 2) and K' (Eq. 9) have very similar values. Thus the difference in concentration between the two neutral π-complexes, **1a** and **5** would result from the aquation equilibrium shown in Eq. 3. As discussed in the Introduction, the value of K_2 (Eq. 3) is less than 0.01 and probably of the order of 10^{-3} so rate increases of a factor of 50–500 would be expected at $[Cl^-] = 0.2$ M. Of course, the actual number is very approximate because **1a** will not have exactly the same reactivity as **5** towards the trans hydroxypalladation shown in Eq. 6. The important point is that the trans hydroxypalladation mechanism would not predict the large retardation actually observed unless there is some basic difference between water and pyridine as neutral ligands. Pyridine does bind more strongly to Pd(II) than does water and use of that fact was made in the present study. What this basic difference effecting



Scheme 5.

reactivity might be is not clear. In discussions of the modes of addition in the Wacker and amination reactions the effect of water and amine ligands are considered to be very similar in that both produce neutral complexes which favor trans addition [5,14]. Thus the trans addition mechanism cannot explain the lowering of the rate by a factor of 750 by replacement of chloride by pyridine. However the cis hydroxypalladation route shown in Eqs. 4 and 5 can rationalize the lowering of rate since coordinated water is specifically required as a reactant for this route.

The same conditions of high $[Cl^-]$ and neutral ligands in the coordination sphere which result in stabilization of the hydroxypalladation adduct can also cause trans addition of H_2O to the intermediate π-complex. Based on the present and previous results in the high chloride system, the most reasonable route appears to be that given in Scheme 5. According to this scheme, the intermediate **5** (Eq. 8), rather than losing another chloride to give the aquo complex **6** (Eq. 9), undergoes trans hydroxypalladation to give the relatively stable adduct, **8**. This adduct can either revert to **5** or, if $CuCl_2$ is present, be intercepted to give 2-chloroethanol. The intermediate **8** is assumed to be in equilibrium with **5** because **8** is stabilized against decomposition to CH_3CHO. This is analogous to the situation with $PdCl_4^{2-}$ at high $[Cl^-]$ shown in Eq. 7. Of course, with ethene the addition–elimination sequence produces no net change. In order to determine the relative values of k_{-1} and k_2 the rates of oxidation and isomerization of an olefin such as allyl alcohol-d_2 (Eq. 7) must be measured at several $[CuCl_2]$.

An interesting mechanistic question which arises is the identity of the intermediate, **5** or **8**, which gives the ethanal product. If the pathway proceeds via **5**, the mechanism would be analogous to that proposed for the reaction at low $[Cl^-]$. This path would involve first replacing a chloride in the coordination sphere with water followed by dissociation of a proton in an equilibrium step in a manner analogous to Eqs. 3 and 4. Then cis attack of hydroxide (Eq. 5) would give the intermediate that would decompose to ethanal. If **8** is the intermediate, the route would be analogous to that proposed to explain trans addition of water (Eq. 6) [5]. Trans equilibrium hydroxypalladation would be followed by loss of another chloride to put water in the coordination sphere. This would provide the labile coordination site necessary for hydride transfer to give ethanal. Both routes would give Eq. 1 as the rate expression. Of course there is always the possibility both mechanisms are operative simultaneously. Studies are underway, using the tetrasubstituted allylic alcohols, **3a** and **3b**, mentioned in the Introduction, to determine the exact mechanism. Kinetics will determine the type of hydroxypalladation which predominates and stereochemical studies using chirality transfer on the exchange will confirm the mode of addition suggested by the kinetics. For example, previously it was found that exchanges that obeyed Eq. 1 underwent cis addi-

tion [9], while those that obeyed Eq. 7 proceeded by trans addition [10].

The increase in 2-chloroethanol yield with increasing $[CuCl_2]$, shown in Table 3, is certainly expected since 2-chloroethanol formation must involve some interaction between $CuCl_2$ and the hydroxypalladation adduct, **8**. The authors are not aware of any similar studies on the effect of $[CuCl_2]$ on 2-chloroethanol yield. However there has been some study of the effect of $[Cl^-]$ on 2-chloroethanol yield at constant $[CuCl_2]$ [4]. Thus at $[CuCl_2] = 4$ M, with no added chloride, the ethanal yield was 97% and the 2-chloroethanol yield 3%. At $[Cl^-] = 10$ M, at the same $CuCl_2$ concentration, the yield of 2-chloroethanol was 63% with the rest being ethanal. These results suggest that increasing the chloride concentration even mildly with the $PdCl_3(Py)^-$ catalyst would give much higher 2-chloroethanol yields at the same $[CuCl_2]$.

In conclusion, this study demonstrates the need for a detailed and accurate knowledge of the mechanism of a catalytic process. Only with such knowledge can the catalyst be modified to give new catalytic chemistry.

4. Experimental section

4.1. Materials

The palladium(II) chloride was purchased from AESAR and the LiCl was purchased from Aldrich Chemical Co. All other chemicals were of reagent grade. Stock solutions of the following compositions were prepared: 0.2 M in Li-$PdCl_3(Py)$, 2.0 M in LiCl, 2.0 M in perchloric acid and 3.0 M in $LiClO_4$. Reaction mixtures were prepared by diluting these stock solutions.

4.2. Physical measurements

All ^1H NMR data were recorded on a Varian VXR 300 NMR spectrometer. GLC analyses were carried out using a Perkin Elmer Sigma 3B gas chromatograph.

4.3. Preparation of potassium trichloropyridine palladate(II), $KPdCl_3(Py)$ [15]

A 9.25 g sample, (28.3 mmol) of K_2PdCl_4 and 2.39 g, (283 mmol) of pyridine were suspended in 100 ml of DMF and stirred at room temperature for 4 h. During this time the starting materials completely dissolved, while KCl precipitated. The solution was then kept in the refrigerator for approximately 2 h to complete the deposition of KCl. The reaction mixture was then filtered and the complex precipitated with an isopropyl alcohol/ether mixture, (1:2, 300 ml).

The product was filtered off and washed with small portions of acetone and ether and dried in a desiccator at room temperature in the presence of $CaCl_2$ followed by P_2O_5 at 110°C under vacuum. The yield obtained was 8.09 g, 86.3%. Mp: 300°C (decomposed).

4.4. Standardization of $KPdCl_3(Py)$ stock solutions [16]

From an unstandardized stock solution of approximately 0.2 M $KPdCl_3(Py)$ in water was pipetted 10 ml of solution. This was diluted to 30 ml of solution with deionized water, followed by 20 ml of 10% HCl solution. To this solution was added excess amounts of 1% dimethylglyoxime in ethanol, and the mixture allowed to stand for 30 min. A golden precipitate appeared. A sintered glass funnel was dried to constant weight at 150°C, and used for filtering this product, which was also dried to constant weight at 150°C. From the weight of the precipitate the concentration of the stock solution was calculated.

4.5. Ethylene uptake experiments

The reactions were run in a creased flask at 25°C and a constant ethylene pressure of 1 atm. The gas uptake was measured by means of gas burets thermostated at the reaction temperature. The reaction flask was a 250 ml two-necked cone-shaped flask with the sides indented at four places to increase stirring efficiency. A magnetic stirring bar was

used for agitation. The apparatus is similar to that previously described [17]. In a typical run the flask containing 50 ml of the reaction mixture was placed in a constant temperature bath and connected to the gas buret. The system was then evacuated for 10 min on the vacuum line with the stirrer running. The stirring was then stopped and the system pressurized to 1.0 atm with ethene. The mercury in the gas buret and the leveling bulb were then equalized, and a reading taken. The stirrer was turned on to start the run. The pressure was kept constant by continuously leveling the mercury in the gas buret and bulb.

The kinetic runs were carried out at a constant ionic strength of 2.0 adjusted with $LiClO_4$ and were 0.2 M in quinone so the Pd(0) formed was continuously reoxidized to Pd(II). Since, in all runs the concentrations of all reactants remained constant, a plot of ethene uptake vs. time gave a straight line. Solubilities were determined by measuring the ethene uptake using solutions with the same composition as the reaction mixtures, but with the palladium(II) ions omitted. The linear zero order rates were converted to 1st order constants in ethene oxidation by dividing by the ethene concentration [3].

For the determination of the much faster initial ethene uptake due to π-complex formation, the reaction mixture was stirred by a four blade stir bar to increase agitation. The volume of solution was increased to 100 ml. The initial gas rapid uptake was over in 30 s. Runs were carried out over a 5 min period, and the plots of ethene uptake vs time, due to the slower oxidation reaction, were extrapolated back to zero time.

The following equation was assumed in calculating the equilibrium constant K_1'.

$$K_1' = \frac{[PdCl_2(Py)(C_2H_4)][Cl^-]}{[PdCl_3(Py)^-][C_2H_4]} \qquad (14)$$

The net ethylene uptake was converted to moles of complex and this was subtracted from total palladium(II) ion concentration to give $[PdCl_3(Py)^-]$. The value of $[Cl^-]$ was:

$$[Cl^-] = \text{Total chloride} - 2[PdCl_2(Py)(C_2H_4)] - 3[PdCl_3(Py)^-]$$

4.6. Analysis of reaction mixtures

The oxidation in the presence of $CuCl_2$ was carried out on a 50 ml scale and allowed to run until the reaction mixture was at least 0.5 M in total oxidation products. The reaction mixture was then extracted with four 2.5 ml aliquots of CD_2Cl_2. The aliquots were combined and dried over anhydrous $MgSO_4$. A portion of the extract was then analyzed by ^1H NMR to obtain the ethanal/2-chloroethanol ratio. Control experiments with simulated reaction mixtures indicated this procedure gave accurate results.

Acknowledgements

Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors also thank Loyola University for the purchase of the VXR-300 NMR used in this work.

References

[1] K. Zaw and P.M. Henry, Organometallics, 11 (1992) 2008.
[2] For general discussion and references, see: P.M. Henry, Palladium Catalyzed Oxidation of Hydrocarbons, D. Reidel, Dordrecht, 1980, p. 41–84.
[3] P.M. Henry, J. Am. Chem. Soc., 86 (1964) 3246.
[4] H. Stangl and R. Jira, Tetrahedron Lett., (1970) 3589.
[5] J.E. Bäckvall, B. Åkermark and S.O. Ljunggren, J. Am. Chem. Soc., 101 (1979) 2411.
[6] K. Zaw, M. Lautens and P.M. Henry, Organometallics, 4 (1985) 1286.
[7] W.K. Wan, K. Zaw and P.M. Henry, Organometallics, 7 (1988) 1677.
[8] N. Gregor, K. Zaw and P.M. Henry, Organometallics, 3 (1984) 1251.
[9] J.W. Francis and P.M. Henry, Organometallics, 10 (1991) 3498.
[10] J.W. Francis and P.M. Henry, Organometallics, 11 (1992) 2832.

[11] P.M. Henry, Palladium Catalyzed Oxidation of Hydrocarbons, D. Reidel, Dordrecht, 1980, p. 76–77.
[12] R.N. Pandey and P.M. Henry, Can. J. Chem., 57 (1979) 982.
[13] R. Jira, J. Sedlmeier and Smidt, J. Justus Liebigs Ann. Chem., 693 (1966) 99.
[14] J.E. Bäckvall, E.E. Björkman, L. Pettersson and P. Siegbahn, J. Am. Chem. Soc., 106 (1984) 4369.
[15] N. Hadjiliadis and G. Pneumatikakis, J. Chem. Soc., Dalton Trans., (1978) 1691.
[16] G.H. Jeffery, J. Basset, J. Mendham and R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, 5th Ed., Longman, London, 1989, p. 463–464.
[17] P.M. Henry, Palladium Catalyzed Oxidation of Hydrocarbons, D. Reidel, Dordrecht, 1980, p. 57.